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13. ABSTRACT *(Maximum 200 Words)*

Direct formation of surface relief gratings at modest intensities on azobenzene polymers has recently been accomplished. Unusual optical erasure of these surface relief gratings was observed. It is found that the optical erasure is dependent on the polarization state of the erasing beam as well as that of the recording beams used to form the gratings. Thus, gratings when formed, memorize the polarization states which create them and influence their erasure behaviors accordingly. Direct transfer of patterns by photoprinting through a phase mask has been achieved.

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Unusual polarization dependent optical erasure of surface relief gratings on azobenzene polymer films.

by

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Abstract

Direct formation of surface relief gratings at modest intensities on azobenzene polymers has recently been accomplished. Unusual optical erasure of these surface relief gratings was observed. It is found that the optical erasure is dependent on the polarization state of the erasing beam as well as that of the recording beams used to form the gratings. Thus, gratings when formed memorize the polarization states which created them and influence their erasure behaviors accordingly. Direct transfer of patterns by photoprinting through a phase mask has been achieved.

Reconfigurable optical recording media[1-7] and direct printing of stable microstructures[8] are of tremendous current interest. In the last decade, polymers containing azobenzene chromophores (guest-host or covalently attached) have been extensively investigated as holographic recording media.[4-7, 9-12] In most of these cases recording and retrieval of optical information resulted from the induced birefringence due to preferential orientation of the chromophores in the medium caused by *trans-cis-trans* photoisomerization. In the past several years, our research group [13-17] as well as that of Natansohn and Rochon [18-20] and more recently Holmes and coworkers [21] have reported recording of large amplitude surface relief gratings on azobenzene functionalized polymers. One-step photofabrication of surface relief gratings at modest light intensities and at temperatures significantly below the glass transition temperature (T_g) of the polymers has been accomplished without any subsequent processing steps. Large surface modulations (>3000 Å) were observed by atomic force microscopy (AFM) at recording intensities as low as a few mW/cm^2. This type of large scale photodriven polymer chain migration responsible for the formation of the surface relief structures at temperatures substantially below T_g is unprecedented and has been found to be unique to azobenzene polymers[16]. Fabrication of surface relief gratings have been demonstrated on a number of azobenzene polymers with the chromophore in the side chain[13-16, 18-21] as well as in the main chain[17]. Surface structures were patterned at room temperature on polymers with T_gs well above 200 °C and with rigid backbones.[17, 22] The formation process of the gratings was found to be strongly polarization dependent[15] and only dependent on the fluence[16]. It has been established that thermal effects do not play an appreciable role in the grating recording process. Such a large nondestructive surface modulation on the films along with the strong polarization dependence of recording was not expected and appears to be

originated from new optically induced processes. A model based on the electric field gradient (of the optical beams) driven transport of the dipolar azo chromophores and the tethered photo-plasticized azobenzene polymers has been developed and adequately explains the polarization dependence of the writing process.[23] The fundamental understanding of the writing process lends itself to the direct photofabrication of photonic components and devices, such as diffractive optical elements that are stable and reconfigurable.

In this letter, we present surprising effects on single beam erasure behavior of previously recorded surface relief gratings. Analogous to the writing process single beam erasure behavior is found to be strongly dependent on the polarization of the erasing beam. What is highly unusual, however, is that, it is also found to be dependent on the state of the polarization of the recording beams which holographically fabricated the gratings in the first place. In other words, these surface relief gratings once formed have memories of the polarization states which created them and exhibit their erasure behavior accordingly. Such memory effects in holographic gratings have not been observed so far. Reproduction and direct phototransfer from a master phase mask has also been accomplished.

Optical erasure of a bulk birefringent grating is easily understood in terms of rerandomization of the chromophore orientation. Erasure of a surface relief grating by optical means must involve large scale polymer transport in a manner analogous to the writing process. The possibility of optical erasure at temperatures substantially below T_g is itself unusual and has not been observed before. For the optical erasure studies, optical quality thin films (0.5 μm thick) of an epoxy based side chain azobenzene polymer[24, 25] were used. Surface relief

gratings were recorded on these azobenzene polymer films at 488 nm. The details of the recording conditions have been discussed elsewhere.[15] The gratings used for these investigations were recorded under the following conditions: (1)*p*-polarization; (2) a linear polarization state which has the plane of polarization making an angle of 45° with respect to *s*-polarization; and (3) circular polarization. The intensity of the recording beams was chosen to be 100 mW/cm^2. The recording time for these gratings was chosen to be 15 minutes to ensure that the amplitude of the surface modulation does not saturate and the surface profile remains fairly sinusoidal. Surface profiles and writing efficiencies were monitored by AFM and diffraction efficiency of a low intensity near-normal incident HeNe laser beam at 633 nm. Within the initial seconds of the recording, preferential orientation of the azobenzene chromophores is built up orthogonal to the polarization of the writing beams leading to a birefringence grating in the polymer film.[4-7, 9-12] The birefringence grating mimics the intensity pattern. For example, with *p*-polarized writing beams, the orientation of the chromophores is expected to be along the grating groove. As the surface relief grating begins to form there is a slight decrease in the diffraction efficiency before it increases further as the grating pattern evolves out of phase with respect to the birefringence grating.[15] These aspects of the recording, net orientation of the chromophores as well as the relief pattern, become part of the recording memory.

Erasure behavior was investigated as a function of time by exposing the recorded gratings to a single laser beam (at the recording wavelength) of a specific polarization at normal incidence. This single erasing beam will interact with the grating and the chromophores will experience a force due to the resulting optical pattern. The polarization state of the erasing beam was chosen

to be either circular or linear (either parallel or perpendicular to the grating grooves). The intensity of the erasing beam was comparable to that of the recording beams and was kept the same for all cases. The erasure process was probed by monitoring the diffraction efficiency of the same HeNe laser beam at 633 nm where the polymer has negligible absorption and has no observable effect on the erasure process. In addition, the surface modulations of the gratings before and after the erasure process were measured by AFM to make sure that the diffraction effects during the erasure experiments were in fact associated with surface relief gratings.

The erasure behavior of the surface relief gratings recorded with *p*-polarized beams are shown in Fig. 1. For these gratings, the erasing beams with all three polarizations lead to a reduction of diffraction efficiency although the erasure rates are different. The erasure rate is most rapid when the polarization is along the grating grooves. AFM scans of the gratings prior to and after the optical erasure clearly show decreases of surface modulations which are completely consistent with the diffraction efficiency data. A significant drop in surface modulation is observed for the grating erased by the beam with polarization parallel to the grating grooves.

Fig. 2 displays the erasure behavior of the surface relief gratings recorded with beams having polarization 45° with respect to *s*-polarization. In this case, again the beam with polarization parallel to the grating grooves is most effective in erasing the grating. However, the erasing beam having polarization perpendicular to the grating grooves leads to a small initial increase in the diffraction efficiency which then remained constant for the duration of the rest of the experiment (2700 seconds). Decreases in surface modulation for the gratings

after the erasure with the erasing beams having polarization parallel to the grating grooves and circular polarization are observed by AFM. For the erasing beam with polarization perpendicular to the grating grooves, AFM scan of the grating after erasing exhibits no change in surface modulation which agrees with the constant diffraction efficiency observed. Thus, one can consider that for an erasing beam with polarization perpendicular to the grating grooves the grating is essentially "fixed" and no erasure will occur in the duration of the experiment. This result has important implications in the use of these gratings as phase masks. Thus, if a grating is written with the appropriate polarization, then one can use this grating as a phase mask to fabricate other gratings on similar polymers and other photoresponsive materials by direct printing without any fear of erasure, provided the correct polarization is selected to illuminate the phase mask.

The erasure behavior of gratings written with circularly polarized light is even more interesting. Fig. 3 depicts the erasure behavior of the three different incident polarizations discussed earlier. As observed in the earlier two cases, the laser beams with linear polarization parallel to the grating grooves and circular polarization erase the grating over a period of time with the linear polarization (parallel to the grooves) erasure being more rapid than circular polarization. However, when "erasure" was attempted with polarization perpendicular to the grating grooves the diffraction efficiency almost doubled the initial value in a period of 2500 seconds. Such polarization dependent increase in diffraction efficiency under erasure has never been observed in holographically fabricated surface relief gratings. AFM scans of the gratings after the optical erasing exhibit decrease of surface modulation for the erasing beams with polarization parallel to the grating grooves and circular polarization. For the erasing beam with polarization perpendicular to the grating grooves, AFM scan of the grating

after exposure reveals a 44% increase in surface modulation which is consistent with the doubling of the diffraction efficiency.

Application of the surface relief gratings as phase masks written with appropriate polarization on the azobenzene functionalized polymer films, to replicate the grating structure on other azo functionalized polymer films have been successfully demonstrated. Fig. 4 shows the AFM images of a phase mask and a replica grating produced from the mask. The period of the produced grating is identical to that of the phase mask, which has resulted from the interference of the zeroth and the first order diffracted beams. Desired modulation depth may be achieved by controlling the degree of exposure.

An exact model for the polarization dependent writing behavior has been developed based on the electric field gradient driven transport of the dipolar azo chromophores and the tethered plasticized azo polymers.[23] Considering the fact that the process of surface relief grating formation is strongly polarization dependent[15] and also that in the process of recording the grating the polymer becomes birefringent with the chromophores preferentially oriented we have all the elements to provide a model for the memory effect and polarization dependent erasure as well. If the incident and the diffracted beams have the optimal polarizations for the formation of surface relief gratings they can interfere and enhance the already existing surface relief grating. It is not surprising that laser beam with polarization parallel to the grating grooves leads to the fastest erasure as it has been shown earlier by Jiang *et al.*[15] that interfering *s*-polarized beams do not form surface relief gratings. Nevertheless the observations reported here pretty much turn the conventional concept of holographic grating erasure topsy-turvy. Instead of erasure in certain situations

we can expect to see considerable enhancement rather than erasure.

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Figure Captions

FIG. 1. The erasure behavior of the surface relief gratings (recorded with *p*-polarized beams) under three erasing polarization conditions: linear polarizations (1) parallel to the grating grooves (solid line) and (2) perpendicular to the grooves (dotted line), and circular polarization (dashed line).

FIG. 2. The erasing processes of the surface relief gratings (recorded with beams having polarization set at 45° to *s*-polarization) under three erasing polarization conditions: linear polarizations (1) parallel to the grating grooves (solid line) and (2) perpendicular to the grooves (dotted line), and circular polarization (dashed line).

FIG. 3. The erasure behavior of the surface relief gratings (recorded with circularly polarized beams) under three erasing polarization conditions: linear polarizations (1) parallel to the grating grooves (solid line) and (2) perpendicular to the grooves (dotted line), and circular polarization (dashed line).

FIG. 4. AFM views of a phase mask and a replica grating. The phase mask with a spacing of 900 nm was fabricated at 488 nm with a polarization set at an angle of 45° with respect to *s*-polarization. The mask was then replicated by photoprinting using a single beam exposure at 514 nm with a polarization perpendicular to the grooves of the mask. There is no erasure of the mask for this polarization.

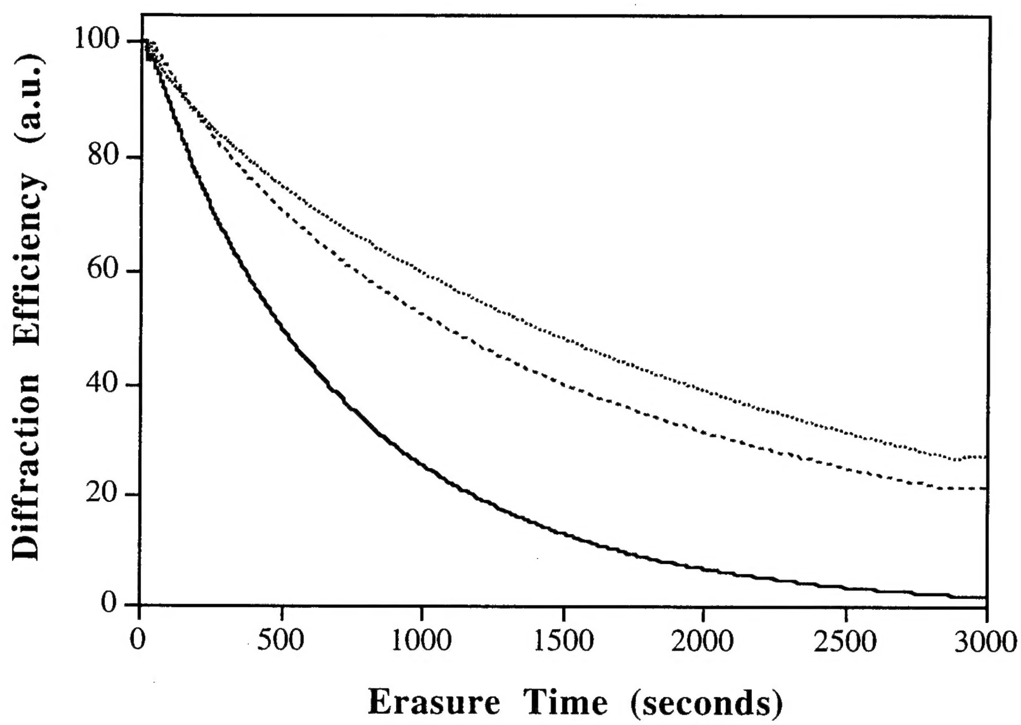

FIG. 1.

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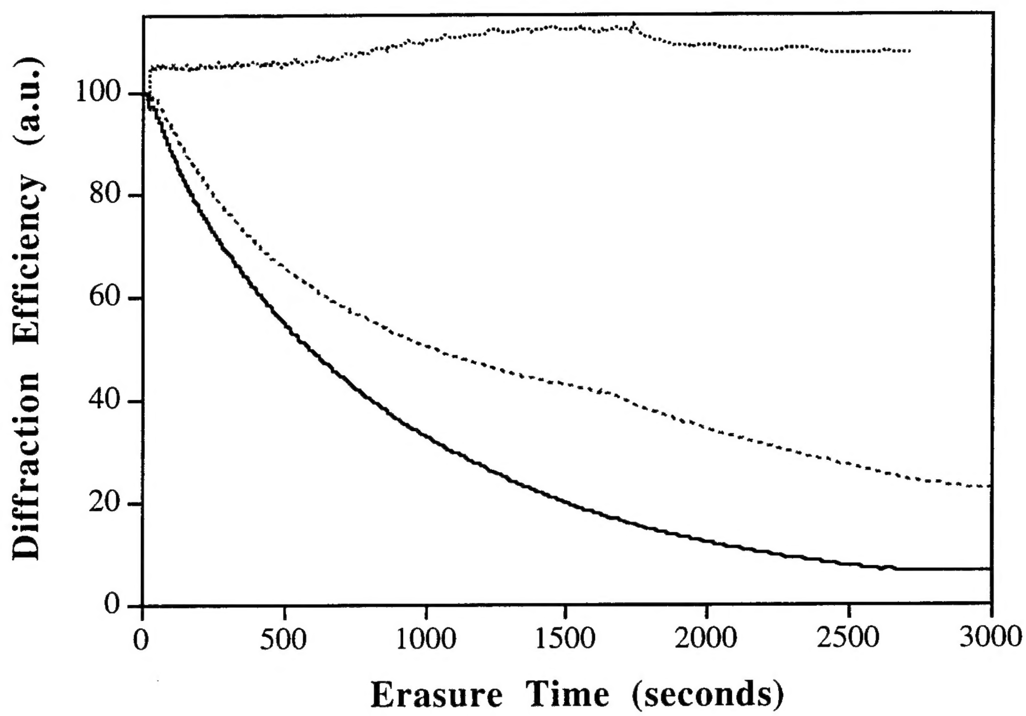

FIG. 2.

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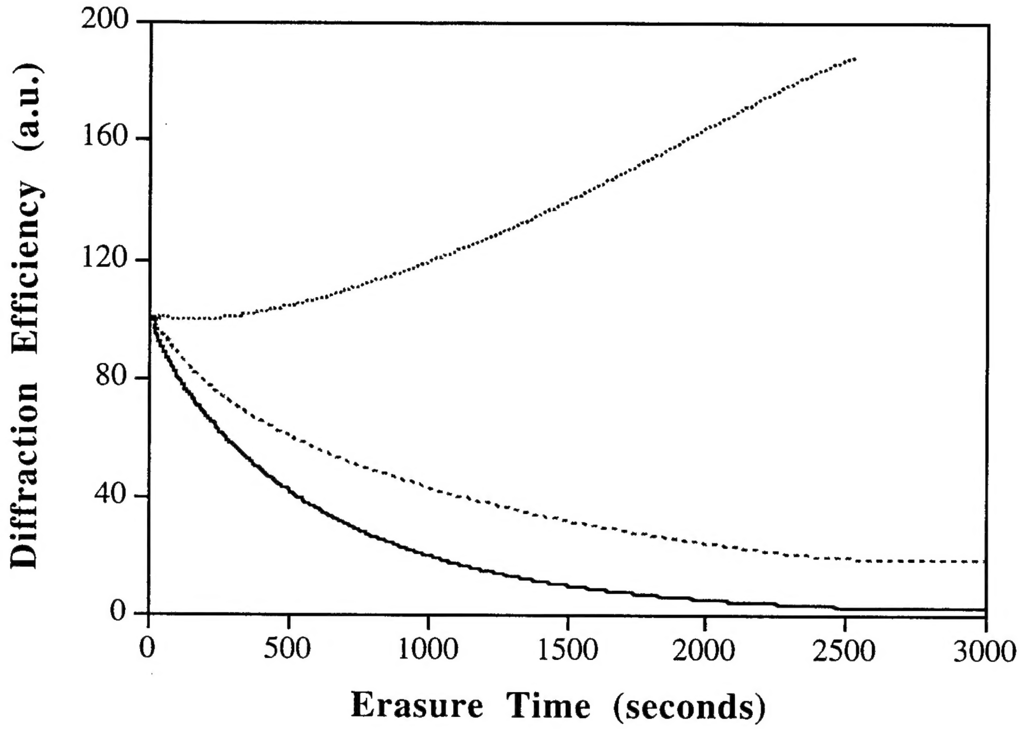

FIG. 3.

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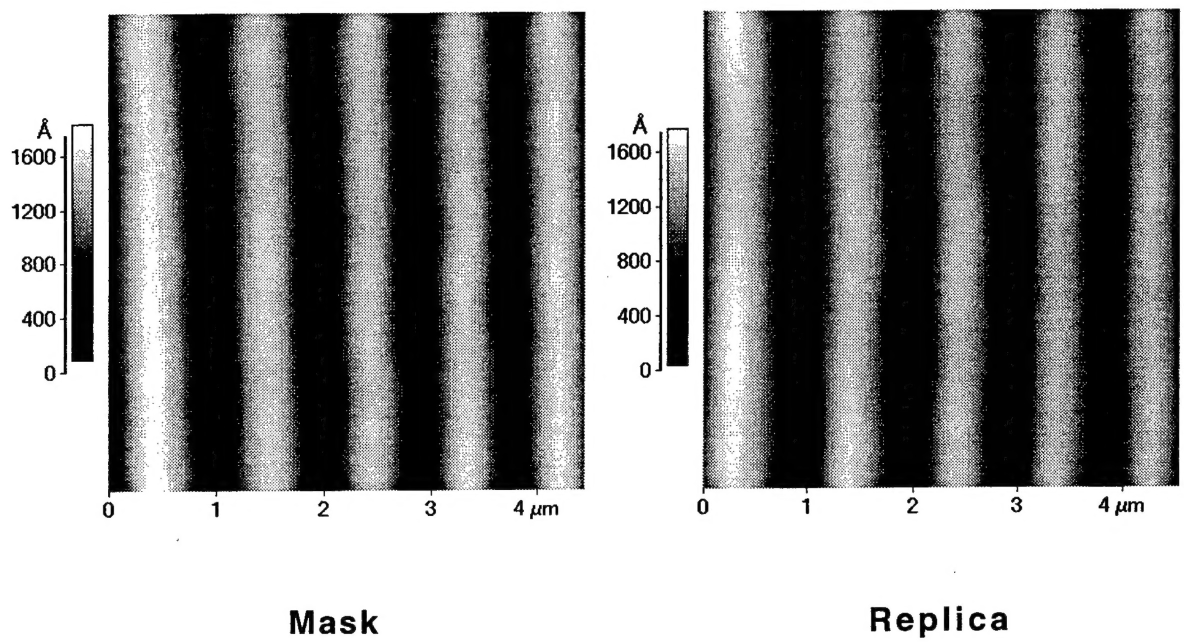

FIG. 4.

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